Manal Shaker,[1] *Ihab Kamel,*[1] *Frank Ko,*[1] *and John W. Song*[2]

R96-86

Improvement of the Interfacial Adhesion Between Kevlar Fiber and Resin by Using R-F Plasma

REFERENCE: Shaker, M., Kamel, I., Ko, F. and Song, J.W., **"Improvement of the Interfacial Adhesion Between Kevlar Fiber and Resin by Using R-F Plasma,"** *Journal of Composites Technology & Research*, JCTRER, Vol. 18, No. 4, October 1996, pp. 249–255.

ABSTRACT: The interfacial adhesion between fiber and matrix has a significant effect on the overall performance of a composite. The necessity of binding the fibers together in a structural composite creates the need for an enhanced interfacial bond between fibers and matrix. One possibility to change the fiber/matrix bond in composite materials is to modify the surface of the reinforcing fiber. One technology useful for this purpose is plasma treatment. This paper discusses optimizing R-F plasma polymerization of allylamine onto Kevlar 29 and KM2 fibers. The treatment was carried out in two steps. First, the fiber was treated with Argon; second, the fiber was treated by allylamine. A method was found such that, under such optimum treatment conditions, the plasma treatment does not adversely affect the mechanical properties of the fibers. This allows flexibility in the tailoring of interfacial properties to optimize the energy absorption capability of the composites. A method was also found that increases interfacial adhesion between PPTA fiber (Kevlar) filament and the matrix as the thickness of the plasma allylamine coating increases.

KEY WORDS: Kevlar fiber, epoxy, plasma treatment, interfacial adhesion, monomer

Surface modification of reinforcement fibers by exposure to certain plasmas appears to have considerable potential as a means to improve the performance of composites [*1*]. Such treatment should not affect the core of the fiber although surface properties are changed.

Although several publications have reported [*1,2*] that the mechanical properties of composites reinforced with plasma treated fibers are enhanced, there has been no study of the impact of fiber surface treatment on the interfacial shear strength [*3*].

Plasma polymerization of a monomer onto the fiber surface is a powerful technique that produces a linked interface. The plasma-produced film layer is pin-hole free, highly cross-linked and is well grafted to the fiber substrate. Functional groups on the surface of the grafted film act as a coupling agent. A further advantage of this technique is fine control over coating thickness. For example, the thickness of the grafted polymer layer produced can be made very small compared to the fiber diameter.

[1]Drexel University, Department of Materials Engineering, Philadelphia, PA 19104.

[2]U.S. Army Natick Research, Development, and Engineering Center, Fiber and Polymer Science Division, Science and Technology Directorate, Natick, MA 01760.

© 1996 by the American Society for Testing and Materials

The plasma polymerization technique has several advantages over conventional coating methods. The strong interfacial bonding between treated fibers and the matrix will provide for effective load transfer and protect the interface from aggressive environmental attacks. Monomer selection for polymerization is based on the functional groups desired and their compatibility with the matrix material.

The current study deals with the modification of Kevlar 29 and KM2 (PPTA) (poly-phenylene terephthalamide) fibers by RF plasma. The objective of this approach is to optimize the bonding between Kevlar 29 and Kevlar KM2 fibers and epoxy resin matrix. The gas media used in the chamber was argon followed by monomer. The effect of plasma treatment on the interface between fiber and matrix materials will be tested by (a) single fiber pull-out and (b) Tensile test of Kevlar fibers yarn.

Optimization of the bonding between Kevlar 29 and Kevlar KM2 and the epoxy resin matrix by RF-Plasma polymerization of the allylamine monomers were investigated.

Technical Approach

Argon Plasma Treatment

Argon plasma etching at 5 min and 50 W for Kevlar 29 KM2 was used. At 30 W, the etching was very slow and lacked uniformity along the fiber length; above 50 W, the plasma power reduced the tensile strength of the fiber that could be due in part to the rapid etching and/or the excessive surface temperature expected when the surface is bombarded by ions and electrons at a fast rate.

Plasma Polymerization and Coating of Allylamine

The Kevlar fibers were first treated with argon plasma for 5 min at 50 W before the vapor of allylamine monomer was introduced into the reactor chamber at the same plasma power level. The monomer flow rate was kept constant at 0.02 g/min, which resulted in a 0.5 Torr reactor pressure. The desired plasma power of 50 W was selected. Treatment time varied from 15 to 45 min. Plasma power was terminated at the end of the treatment.

SEM Examination

The surface morphology of the treated fibers was examined under the scanning electron microscope (SEM) (JOEL model JSM-35CF). Fibers were coated with a vapor-deposited thin layer of gold to induce conductivity before examination under the SEM.

The Use of RF Plasma

Plasma is a partially ionized gas composed of ions, electrons, and neutral species. It is a state of matter that can be created by such diverse techniques as flames, electrical discharge, electron beams, lasers or nuclear fusion. Plasma created in a reactor chamber is used to modify the surface of materials. In this technique, free electrons acquire energy from the imposed electric field and lose it through collisions with neutral gas molecules. These collisions produce metastable atoms, free radicals, ions, and so forth that act as precursors to unique and novel chemical reactions. The plasma created is characterized by electron energies in the range of 1 to 10 eV and by electron densities in the range of 109 to 1012 cm^{-3}. It is also characterized by a lack of thermal equilibrium. While the bulk temperature is near ambient temperature (300 to 600°K), the temperature of free electrons in the ionized gas can be 10 to 100 times higher. This type of plasma is referred to as "cold plasma."

In the work done by Krishnamuthy and Kamel [*4*], the surface of the glass fiber was modified by means of plasma treatment. In this technique, the fiber surface was first treated with chemically nonreactive plasma (argon gas), then a vapor of organic monomer (allylamine) was introduced to form a thin layer of highly cross-linking polymer film on the fiber surface. Most of the organic compound vapors tended to form a film on the surface subject to the glow discharge depositing covalently bonded polymer surface on the substrate. Deposition of these films on the surface of the glass fiber resulted in surface modification and improved the compatibility between fibers and the matrix material. The biggest advantage of this technique is the fact that plasma polymerization only changes the surface properties without affecting the bulk properties of the substrate. This is due to the very low penetration range of plasma polymerization. The plasma process is called competitive ablation and polymerization (CAP) Figure 1 shows the overall mechanism of glow discharge polymerization [*5*].

Experimental Procedures

Materials

150 den Kevlar 29 and KM2 yarns were obtained from the Du Pont company. The individual filaments had an average diameter of 11 μm. Laboratory grade argon gas from Airco was used for the plasma treatment. Epoxy resin Epon and curing agent w obtained from Shell Chemical Company. Allylamine with 9 purity from Aldrich Chemical Company, Inc. was the selec monomer for the plasma coating.

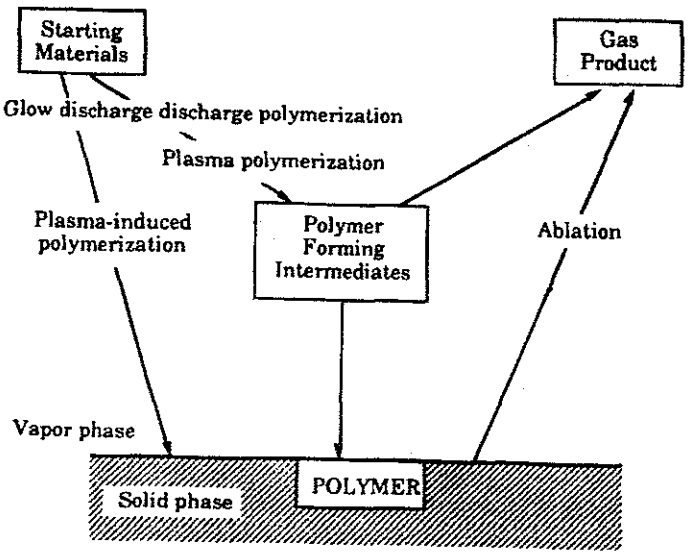

FIG. 1—*Mechanism of plasma polymerization.*

Tensile Tests at Room Temperature

Yarns were tested at a gage length of 25 cm. Ten specimens gage length were tested for different treatment of yarns. The t specimen preparation included mounting the yarn on a cardbo frame with no twist added. The mounted yarns were sandwic at the end tab parts with another piece of cardboard and gl together with a structural adhesive (EA 9303, manufactured the Dexter Corporation, Hysol Division). The end tabs of specimens were dried under pressure for 24 h. The neck par the paper frame was cut after the specimen was mounted in grips before testing.

Tests were performed on a model 1127 Instron tester un standard testing conditions at 70°F, 65% relative humidity. Wed section friction grips were used for all the tests. Test specificati for gage length are as follows: gage length 250 mm; full s load 50 Kg; cross head speed 100 mm/min; and linear den 1500 den.

Fiber Handling

This process was developed to handle the fibers during pla treatment and the molding of end tabs in preparation for test The Kevlar fibers were stretched on a 10 by 4 cm vinyl fr with a centered 7 by 3 cm cut out section. The fibers were gl to the frame using vinyl end tabs and cyanoacrylate glue as sh in Fig. 2.

Sample Preparation and Testing

In order to measure the interfacial shear strength between Kevlar and the epoxy matrix, a fiber pull-out test was used In this test, the fiber end of the test sample was placed in 1-mm deep silicone rubber cavity that was filled with epoxy r At the other fiber end, extra fiber length was packed into a 3 20 mm silicone rubber mold; the fiber ends were 2 cm a Epoxy resin was poured into the mold cavities and allowed to for 36 h at room temperature. After removal of the cured ep from the molds an aluminum piece of 15 by 15 mm was attac to the 2-mm thick end using a cyanoacrylate adhesive. The sar was gripped during testing from this aluminum part, to pre

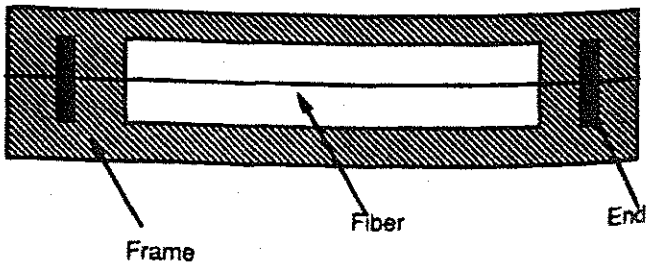

FIG. 2—*Single filament pull-out test.*

distortion of the thin epoxy test section and pulled at the rate of 1 mm/min. Figs. 3 shows the overall shape of the test sample.

Results and Discussion

Plasma Treatment

Plasma treatment of Kevlar 29 and Kevlar KM2 is classified into two steps as follows.

Argon Plasma Treatment—Plasma etching of the fiber surface was found to be sensitive to the presence of oxygen. Therefore, care was taken in purging the reaction chamber three times with argon before starting the plasma etching process. The plasma power selected for the treatment was chosen to be 50 W. At 30 W the etching was very slow and lacked uniformity along the fiber length. Above 50 W, the tensile strength of the fiber was reduced; for example, at 70 W power and 5 min exposure time, the tenacity of Kevlar 29 fibers dropped by 30% of the as-received values shown in Table 1. At higher power, the degradation in strength could be due to rapid etching at higher temperature that may result from a faster rate of bombardment by ions and electrons of the fiber surface. Changes in the fiber surface morphology as a result of argon plasma etching are shown in Fig. 13 (Kevlar 29) and 7 (Kevlar KM2).

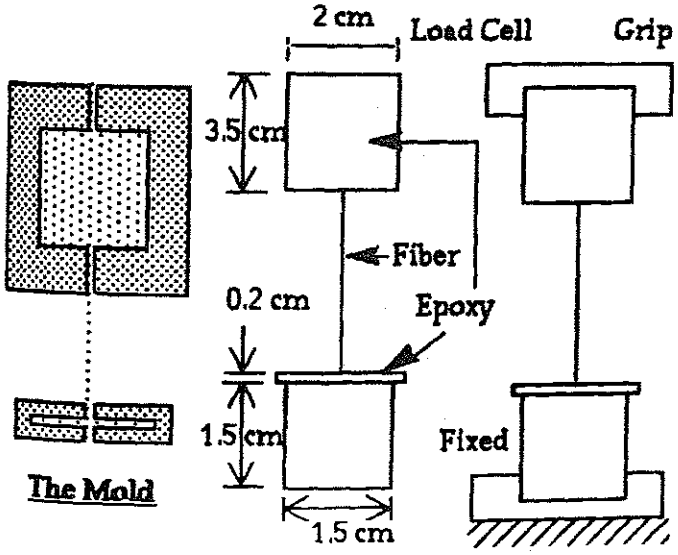

FIG. 3—*Schematic of single filament pull-out test.*

The argon plasma treatment decreased the Kevlar fibers' apparent diameter (Fig. 7).

Allylamine Plasma Treatment—SEM micrographs of allylamine plasma coated fibers showed an increase in the fiber diameter change in the surface texture. It can be seen from Figs. 14 (Kevlar 29) and 6 (Kevlar KM2) that after 15 minutes of allylamine plasma coating, the overall diameter increases by 10%. This coating can be increased by increasing the monomer polymerization time to a maximum of up to 50% of original diameter after 45 minutes of coating (as shown in Figs. 10 and 17 for Kevlar KM2 and K29 respectively). The appearance of surface microstructures was changed after 15 min of plasma treatment. However after 30 to 45 min of treatment, a very smooth thick coating covered the original morphology, causing drawing marks of etched surface defects to disappear from the surface.

Table 1 shows measured tenacity, load, breaking elongation and modulus of coated vs. uncoated Kevlar. The tenacity of allylamine-coated Kevlar 29 and Kevlar KM2 at 15 minutes and 50 W increased slightly over the untreated fiber, due to the chemical bond between the allylamine-plasma and the sizing agent. It is also interesting to observe that, after 30 and 45 minutes of plasma treatment, the tenacity drops from 17.29 g/den to 15.36 g/den-approximately the same tenacity as the sizing. During tenacity measuring, the thick layer of plasma treatment I. E. after 30, 45 min of coating cracked and separated from the fiber surface. This means that the bond between the fiber and the sizing agent was not as strong as the bond between the sizing agent and the allylamine.

Table 2 shows measured tenacity, load, breaking elongation and modulus vs. the allylamine coating for Kevlar KM2 and K29 after removing the sizing. The tenacity decreased after the sizing was removed by soaking the fiber as received in 1:1:1 trichloroethane, and the diameter for single fiber decrease as in Figs. 6 and 12 for Kevlar KM2 and Kevlar 29. Yarn sizing aids in load transfer and lowers inter-fiber frictional stress. When the sizing is removed, the filaments in the yarn are no longer bound together. When loaded, instead of acting as a cohesive bundle, the filaments break individually. Once a filament breaks, it ceases to contribute to yarn strength. In Table 1, it is shown that tenacity increases rapidly with up to 15 minutes of plasma treatment, while the tenacity of

TABLE 1—*Measured tenacity, load, breaking elongation and modulus of coated versus uncoated Kevlar.*

Type	Tenacity, g/den	Deviation	Load, Kg	Deviation	Breaking Elongation, %	Deviation	Modulus, gm/den	Deviation
K29 original fiber	16.47	0.881	24.71	1.322	2.68	0.111	630.1	2.13
K29 remove sizing	15.35	2.075	23.03	3.11	2.64	0.133	604.6	8.2
K29 after treat original[a]	17.29	0.095	25.95	1.43	2.75	0.168	644.6	1.64
K29 after treat original[b]	15.36	0.72	23.04	1.08	2.58	0.22	603.2	2.24
K29 after treat original[c]	14.09	0.93	21.13	1.4	2.58	0.34	567.5	2.9
KM2 original fiber	19.2	1.42	28.8	2.13	3.132	0.231	621.7	1.43
KM2 remove sizing	18.32	1.15	27.48	1.73	3.035	0.1996	609.3	2.53
KM2 after treat remove	20.12	1.07	30.19	1.6	3.126	0.1904	636.9	2.19
KM2 after treat original[a]	19.28	1.05	28.91	1.58	3.129	0.162	634.2	2.81
KM2 after treat original[b]	17.2	1.11	25.8	1.17	3.04	0.28	573	2.337
KM2 after treat original[c]	17.85	1.64	26.78	2.46	3.27	0.55	559.7	2.88

[a]Treatment with argon at 5 min 50 w and allyamine 15 min 50 w power.
[b]Treatment with argon at 5 min 70 w and allyamine 30 min 50 w power.
[c]Treatment with argon at 5 min 70 w and allyamine 45 min 50 w power.
[d]Number of observation = 20.

TABLE 2—*Measured tenacity, load, breaking elongation and modulus versus the allylamine coating for Kevlar KM2 and K29 after remo the sizing.*

Type	Tenacity, g/den	Deviation	Load, Kg	Deviation	Breaking Elongation, %	Deviation	Modulus, gm/den	D
K29 original fiber	16.47	0.8881	24.71	1.322	2.68	0.111	630.1	
K29 remove sizing	15.35	2.075	23.03	3.11	2.64	0.133	604.6	
K29 after treat remove[a]	14.79	1.88	22.19	2.84	2.16	0.204	578.6	
K29 after treat remove[b]	17.62	0.887	26.42	1.3	2.82	0.164	648.5	
K29 after treat remove[c]	16.14	2.89	24.2	4.33	2.49	0.601	667.5	1
K29 after treat remove[d]	16.95	1.71	25.43	2.57	2.69	0.723	644.4	
KM2 original fiber	19.2	1.42	28.8	2.13	3.132	0.231	621.7	
KM2 remove sizing	18.32	1.15	27.48	1.73	3.035	0.1996	609.3	
KM2 after treat remove[b]	20.12	1.07	30.19	1.6	3.126	0.1904	636.9	
KM2 after treat remove[c]	19.18	0.63	29.77	0.94	3.06	0.208	632.4	
KM2 after treat remove[d]	18.34	1.26	27.851	1.89	3.11	0.321	597.5	

[a]Treatment with argon at 5 min 70 w and allyamine 15 min 50 w power.
[b]Treatment with argon at 5 min 50 w and allyamine 15 min 50 w power.
[c]Treatment with argon at 5 min 70 w and allyamine 30 min 50 w power.
[d]Treatment with argon at 5 min 70 w and allyamine 45 min 50 w power.
[e]Number of observation = 20.

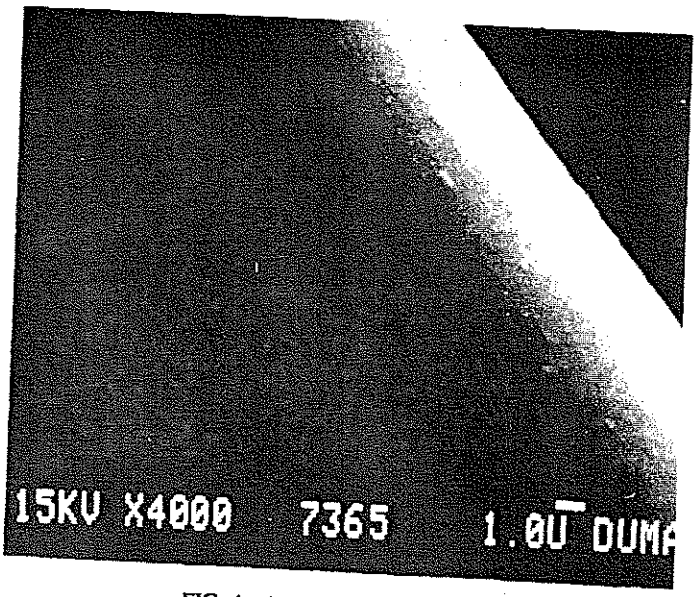

FIG. 4—*Untreated Kevlar KM2.*

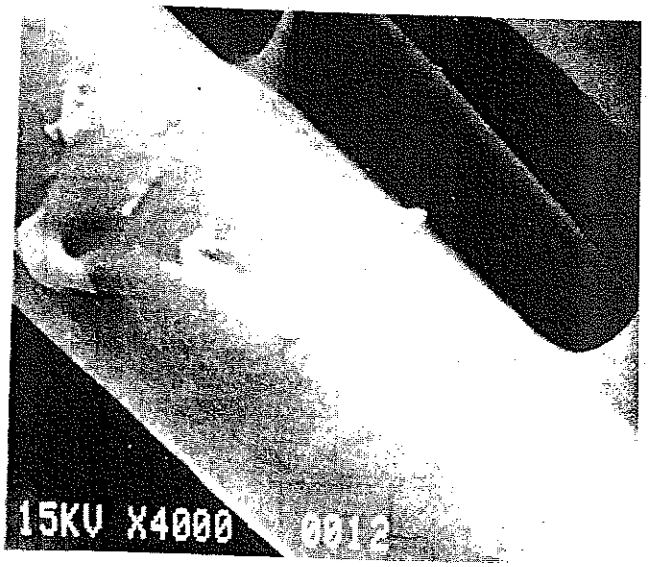

FIG. 5—*Kevlar KM2 after 7 min of trichloroethane treatme remove sizing.*

Kevlar 29 and KM2 with 30–45 minutes plasma treatment remains unchanged with values very similar to the original fiber.

At higher reaction times, a multilayer coating is formed (as shown in Figs. 9, 11, 16, and 17). As the bond between layers of allylamine is not as strong as that between allylamine and fiber, the overall tenacity may decrease or remain the same. This behavior may reflect that the bonding between Kevlar and allylamine is stronger than the bonding between two molecules of allylamine in a multilayer plasma treatment. The allylamine chains, in this case, are able to slip under the localized stress over neighboring chains, which will break and produce molecular flaws, further enhancing stress inhomogenity and leading progressively to catastrophic rupture. When measuring tenacity, the thick layer of plasma cracked and the multilayer coating separated from the yarn. This means that the role played by bonding between fiber and monomer is more apparent.

Interfacial Testing

A trial was made to modify the surface of a PPTA fiber. Tables 3 and 4 show the pull-out load when one end of the PPTA fiber

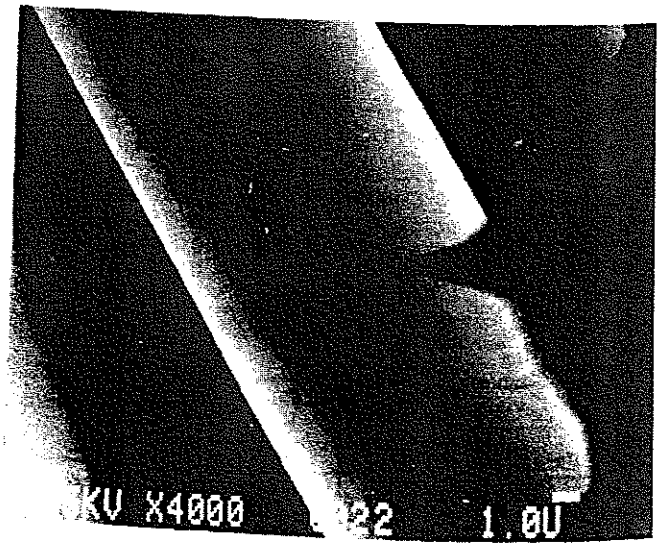

FIG. 6—*Kevlar KM2 after 30 min of trichloroethane treatment.*

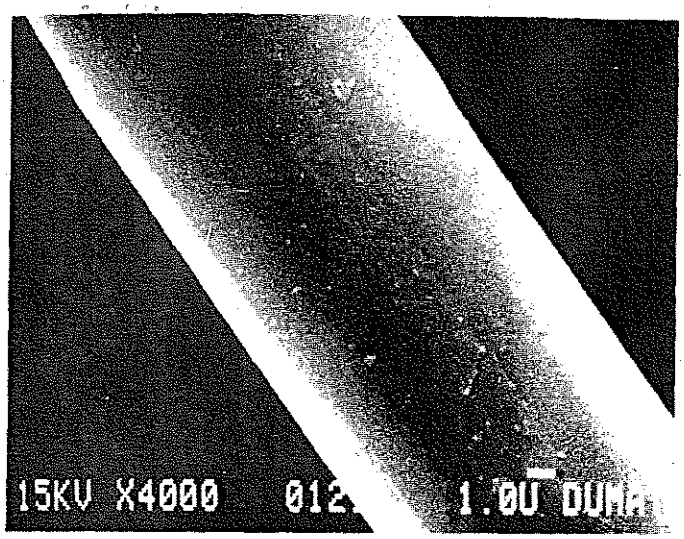

FIG. 7—*Kevlar KM2 after argon treatment (5 min at 70 W).*

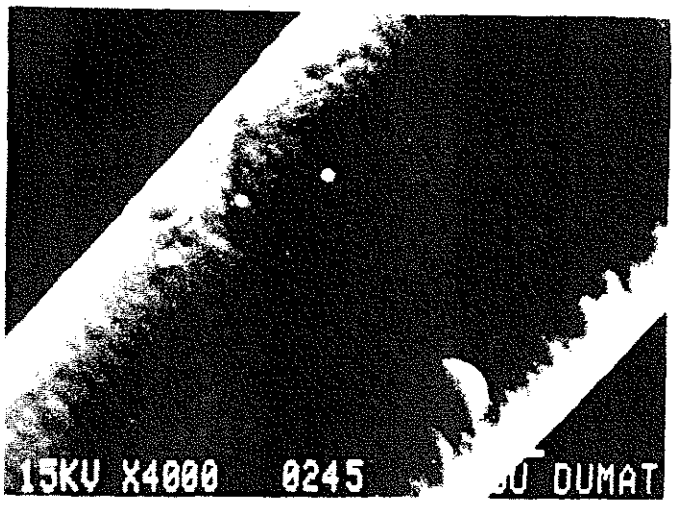

FIG. 10—*Kevlar KM2 after allylamine treatment (45 min at 50 W).*

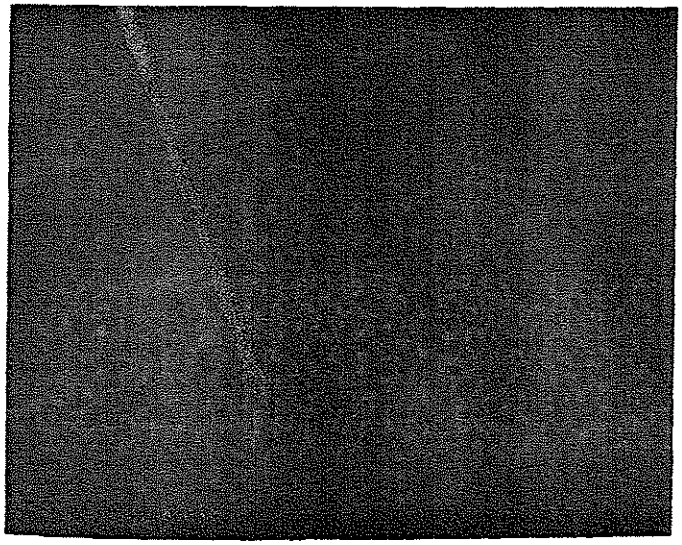

FIG. 8—*Kevlar KM2 after allylamine treatment (15 min at 50 W).*

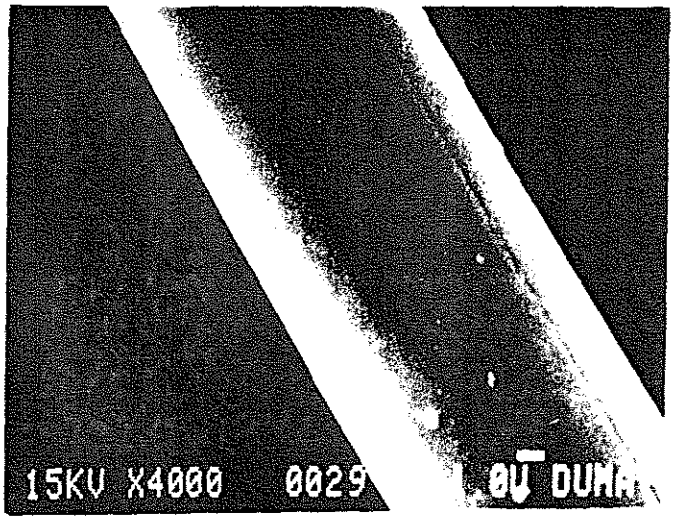

FIG. 11—*Untreated Kevlar 29.*

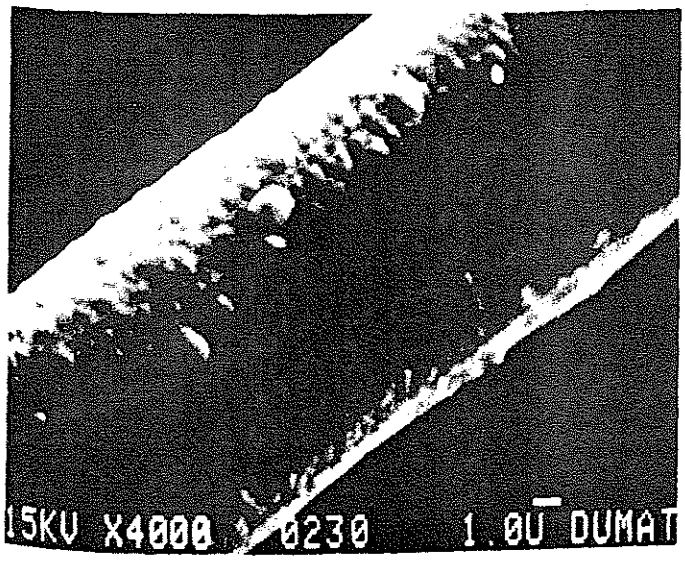

FIG. 9—*Kevlar KM2 after allylamine treatment (30 min at 50 W).*

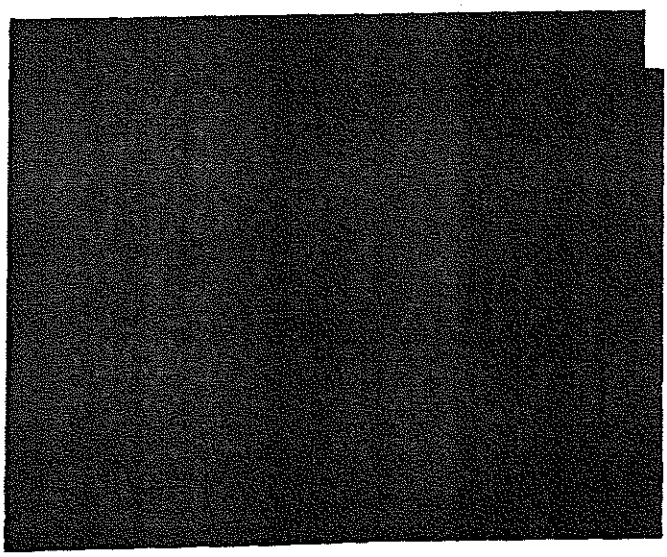

FIG. 12—*Kevlar 29 after 30 min of trichloroethane treatment.*

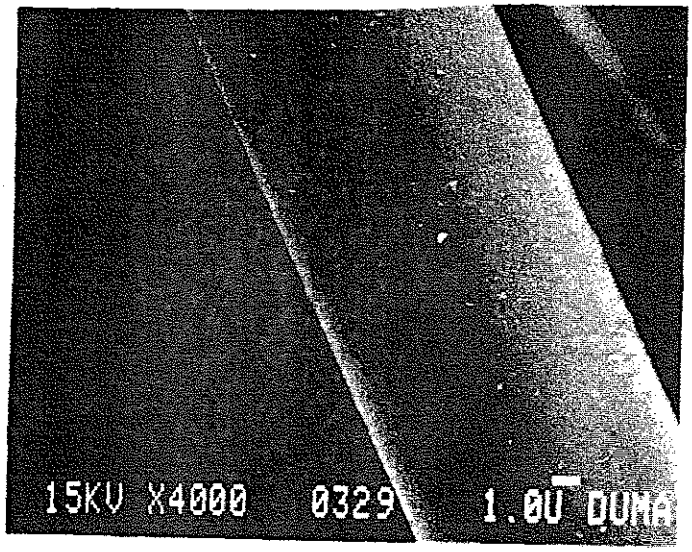

FIG. 13—*Kevlar 29 after argon treatment (5 min at 70 W).*

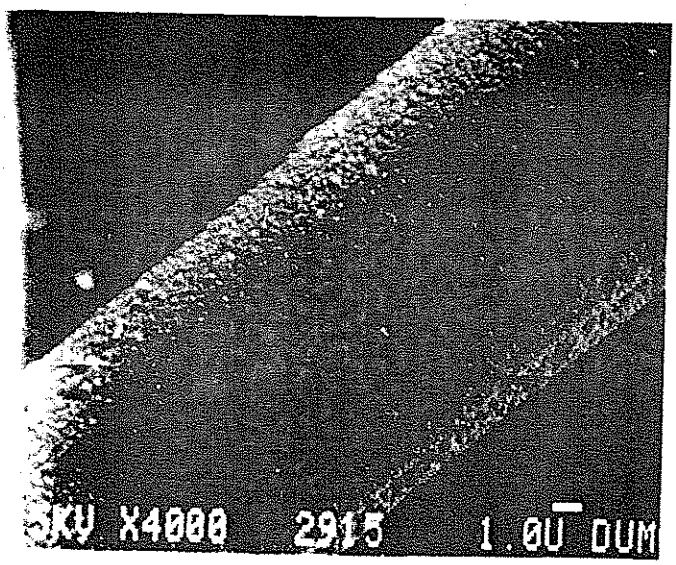

FIG. 14—*Kevlar 29 after allylamine treatment (15 min at 50 W).*

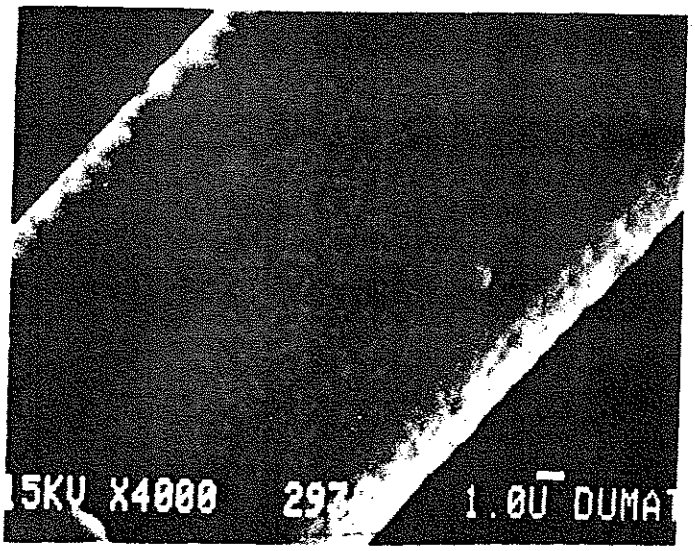

FIG. 15—*Kevlar 29 after allylamine treatment (30 min at 50 W).*

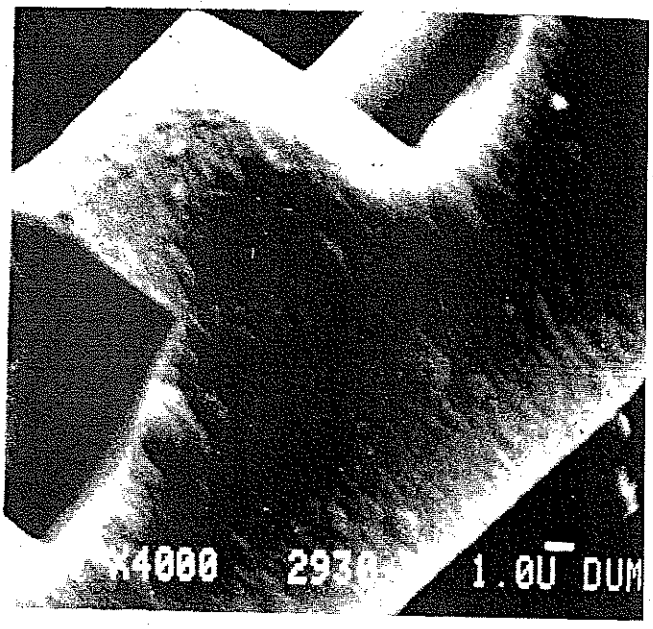

FIG. 16—*Artificially cracked Kevlar 29 after allylamine treatment min at 50 W).*

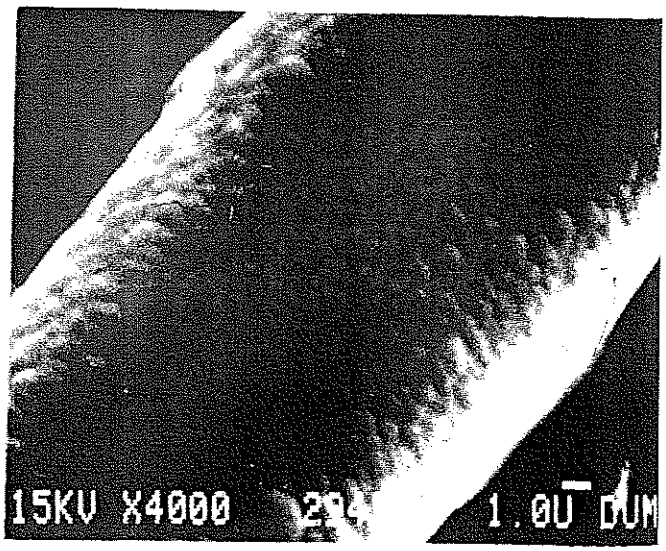

FIG. 17—*Kevlar 29 after allylamine treatment (45 min at 50 W).*

was embedded in an epoxy matrix. From the pull-out load, t average shear at the interface between the fiber and matrix w calculated.

As shown in Tables 3 and 4, the untreated Kevlar fibers ha a very low level of adhesion to epoxy resin (0.24–0.28 MPa). T allylamine plasma treatment of Kevlar fiber increased adhesi up to 0.49–0.54 MPa after 45 min treatment, which is an increa

TABLE 3—*Interfacial shear strength τ versus polymer plasma treatment time for Kevlar KM2.*

Treatment Time, min	Diameter, mm	Pull-Out Load, N	Average Shear Strength, τ, MPa	Fraction Increase in Shear Strengt τ/τ 0
0	0.010	0.284	4.522	1
15	0.011	0.323	4.675	1.033
30	0.012	0.480	6.369	1.408
45	0.0152	0.549	5.751	1.271

TABLE 4—*Interfacial shear strength τ versus polymer plasma treatment time for Kevlar 29.*

Treatment Time, min	Diameter, mm	Pull-Out Load, N	Average Shear Strength, τ, MPa	Fraction Increase in Shear Strength, τ/τ_0
0	0.010	0.245	3.901	1
15	0.011	0.313	4.530	1.61
30	0.015	0.392	4.161	1.066
45	0.015	0.480	5.095	1.306

90–92% over the untreated fibers. It was found that as plasma ating time increased, adhesion increased. This gives evidence t plasma treatment of fiber is a very good tool for enhancing interfacial adhesion between PPTA fiber and matrix.

Conclusions

In this study, PPTA fibers (Kevlar) were modified using an RF-plasma treatment. Tests of the interfacial properties of the treated fibers were performed in order to optimize treatment conditions. The results of this study are summarized below:

- RF-plasma was effective in enhancing the fiber-matrix interfacial adhesion when allylamine was coated to fiber surface. The interfacial shear strength between allylamine plasma coated Kevlar 29 and Kevlar KM2 fibers and matrix material showed five fold increase over untreated fibers.
- The tenacity of argon/allylamine treated fibers yarn is optimal at 5 min and 50 W argon plasma etching followed by 15 min and 50 W of allylamine plasma coating.
- Interfacial adhesion between PPTA fiber (Kevlar) filament and matrix increases with increasing plasma coating. This holds great promise that the impact resistance of the composite structure will be improved, which is the main goal of the present study.

Acknowledgment

The authors gratefully acknowledges the financial support for the project from the U.S. Army Natick Research, Development & Engineering Center, Natick Massachusetts.

References

[1] Kaplah, S. L., Rose, P. W., Nguyen, H. X., and Chang, H. W., Proc. 33rd. International SAMP Symposium, 1988, p. 551.
[2] Nguyen, H. X., Weedom, C. C., and Chang, H. W., Proc. 34th International SAMPE Symposium, 1989, p. 1603.
[3] Gaur, U., Desio, G. P., and Miller, B., Proc. of SPE ANTIC '89, 1989, p. 1513.
[4] Krishnamurthy, V., "RF Plasma Modification of Glass Fiber-Polyphenylene Sulfide Interface," Ph.D. Thesis, Drexel University, Philadelphia, PA, 1988.
[5] Yasuda, H., *Plasma Polymerization*, M. Shen and A. T. Bell, Eds., ACS Symp. Ser., Vol. 108, 1979, pp. 37–43.
[6] Rostami, G., "Surface Modification, Interfacial Testing and Matrix Processing of Fiber Reinforced Composites," Ph.D. Thesis, Drexel University, Philadelphia, PA, 1988.